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KINETICS OF SOME METAL ATOM AND METAL FLUORIDE OXIDATION REACTIONS RELEVANT TO AIR FORCE TECHNOLOGY DEVELOPMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This experimental work provides kinetic data on metal oxidation reactions for rocket propulsion and ramjet technology programs using the HTFFR (high-temperature fast-flow reactor) technique over the temperature range 300 to 1900 K. Mechanisms and rate coefficients were obtained from optical measurements of the consumption of metal atoms or metal monoxide radicals, as functions of pressure, oxidizer concentration, reaction time, and temperature.

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(Block 20 continued)

Rate coefficient measurements on the reaction of aluminum atoms with nitrogen trifluoride were made over the range 300 to 1000 K, and an Arrhenius expression derived. Above 800 K, gas chromatographic measurements show a thermal decomposition of the trifluoride. Experiments on aluminum monoxide (AlO) reactions indicate that the O-AlO bond strength is probably greater than 126 kcal per mol. Magnesium atoms appear to react with molecular oxygen at 1900 K. Tests of means to vaporize elemental boron are reported. Thermal and microwave discharge dissociation of diborane and boron trichloride produce small quantities of atomic boron; these methods appear more suitable for generating boron monohalides or boron monoxide (in the presence of molecular oxygen).

The accuracy of kinetic measurements on metal atoms at elevated temperatures is the subject of two of the publications resulting from this work. In one of these publications, HTFFR and other techniques for the study of gas-phase oxidation reactions are critically reviewed.

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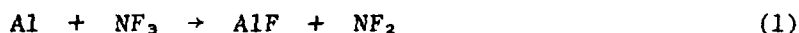By_____
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I. INTRODUCTION - RESEARCH OBJECTIVES

Several Air Force efforts require reliable quantitative kinetic data on the formation of metal oxides, halides, and oxyhalides. Specifically, development of advanced rockets utilizing fluorinated solid propellants loaded with Al and/or B require data on Al and B oxidation by halogen and oxygen species and on the shift reactions of the halides and oxyhalides with (atmospheric) O_2.[1-3] Ramjet technology development requires knowledge of Mg and B oxidation by O_2.[3,4]

In this work the unique capabilities of the AeroChem high-temperature fast-flow reactor (HTFFR) were utilized to provide these kinetic data. The HTFFR, which is essentially a heated flow tube, is capable (in its various modifications) of providing kinetic measurements on elementary gas-phase chemical reactions in the approximate temperature range of 300 to 1900 K. As an experimental tool, the HTFFR allows for independent control of reaction time, pressure, reactant concentrations, and temperature.

For work on this contract, studies of four reactions were considered to be germane to the general objectives stated above:

$$Al + NF_3 \rightarrow AlF + NF_2 \tag{1}$$

$$AlF + O_2 \rightarrow AlOF + O \tag{2}$$

$$Mg + O_2 \rightarrow MgO + O \tag{3}$$

$$B + O_2 \rightarrow BO + O \tag{4}$$

Reactions (1), (3), and (4) are archetypes selected to provide fundamental information on the isolated, elementary oxidation reactions of metal atoms. They may be considered as steps in a series of oxidations leading to heat release and the production of particulate Al_2O_3, MgO, and B_2O_3 from solid rocket motors and ramjets. Reaction (2)* and our previous study[1] of the reaction

$$AlO + O_2 \rightarrow AlO_2 + O \tag{5}$$

can be considered as examples of the subsequent shift reactions in the oxidative sequence. In a programmatic sense, the studies of these reactions are aimed at providing the rate coefficients needed to make an accurate estimate

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* No experimental work on this reaction was undertaken in the present effort.

of the rates and locations of chemical heat release and of particulate forma-
tion in practical devices, and at elucidating likely mechanistic steps in
these processes.

The progress of the work is summarized in the abstracts of the publica-
tions which have resulted from this work (Section II). In addition, a substan-
tive summary of work which will be submitted for publication and work not yet
complete enough for publication is given in Section III.

II. CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS

1.[*] A. Fontijn, "High-Temperature Fast-Flow Reactor Studies of Elementary
Reactions," High Temperature Metal Halide Chemistry, D.L. Hildenbrand and
D.D. Cubicciotti, Eds. (The Electrochemical Society, Princeton, 1978)
p. 484.

A unique experimental method is described for providing information on
the kinetics of individual elementary reactions of neutral metallic species
as a function of temperature. This high-temperature fast-flow reactor (HTFFR)
technique has allowed the study of oxidation reactions of refractory metal
atom and metal oxide species from about 300 to 1900 K by a single experimental
method, thereby overlapping the temperature domains of traditional near room
temperature techniques and flames and shock tubes. The technique, some signi-
ficant results, and its extension to measurements on chemiluminescent and elec-
tronic excitation quenching reactions are briefly reviewed. The significance
of the results for practical systems is pointed out.

2. A. Fontijn and W. Felder, "Factors Affecting the Accuracy of Rate Coeffi-
cients of Metal Atom Oxidation Reactions in Heated Flow Tubes," The Jour-
nal of Physical Chemistry 83, 24 (1979).

Metal atom oxidation reactions have been studied over the 300-2000 K
temperature range. The factors determining the currently achievable accuracy
of 40-70% for the overall rate coefficient measurements of such reactions are

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[*] The publications marked with * cover several topics, not all of which are
pertinent to this contract. Accordingly, they were only partially supported
by this contract.

discussed. Particular consideration is given to the influences of the systematic uncertainties involved in temperature determinations and in the flow profile (reaction time) factor at the relatively high pressures and average gas velocities required for the kinetic measurements. Compared to most regular flow tube studies of nonrefractory species the use of these higher T, P, and $\bar{v}$ has an adverse effect on accuracy; however, it is also shown that the higher T and P increase the accuracy of relative and absolute atom concentration determinations by atomic absorption measurements.

3.[*] A. Fontijn, "Studies of the Elementary Reaction Kinetics of High-Temperature Species Using Optical Measurement Techniques," 10th Materials Research Symposium. Characterization of High Temperature Vapors and Gases, J.W. Hastie, Ed., National Bureau of Standards, Special Publication 561 (1979).

A unique experimental method is described for providing information on the kinetics of individual elementary reactions of neutral metallic species (free atoms and diatomic radicals) as a function of temperature. This high-temperature fast-flow reactor (HTFFR) technique has allowed the study of oxidation reactions of refractory metal atom and metal oxide species from about 300-1900 K by a single experimental method, thereby overlapping the temperature domains of traditional near room temperature techniques and flames and shock tubes. The technique, which uses absorption and fluorescence measurements of the consumption of the metallic species, allows for independent variation of temperature, pressure, reactant concentrations, and reaction time. Some significant results, and an extension to measurements on chemiluminescent and electronic excitation quenching reactions are discussed. A brief comparison is made to other techniques for obtaining information on homogeneous gas-phase reactions of such metallic species. Adaptation of the heated reactor technique to determine the temperature dependence of rate coefficients of elementary reactions of hydrocarbons using high temperature photolysis (HTP) in a static mode is discussed.

4.[*][†] A. Fontijn and W. Felder, "High Temperature Flow Tubes. Generation and Measurement of Refractory Species," Reactive Intermediates in the Gas Phase: Generation and Monitoring, D.W. Setser, Ed. (Academic Press, New York, 1979).

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II. HTFFR (High-Temperature Fast-Flow Reactor) Techniques
     A. General Description and Procedures
     B. The Reactors and Their Operation; Metal Evaporation
     C. Atomic Concentration Measurements
     D. Flow Considerations
     E. Accuracy
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     A. Beam Studies with Luminescence Detection
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     C. Traditional High Temperature Techniques
     D. Photolytic Techniques
     E. Miscellaneous Techniques
IV. Conclusions
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III. ADDITIONAL FINDINGS AND ACCOMPLISHMENTS

A. THE Al/NF₃ REACTION[‡]

This reaction has been the subject of our recent investigations. Its rate coefficient has been measured in the range 300-1000 K. Above 800 K, NF_3 decomposes rapidly under the experimental conditions, so that rate coefficients determined in the 800-1000 K range represent reactions of Al with both NF_3 and its thermal decomposition fragments. In the 300-800 K range, the measurements (summarized in Table I and Fig. 1) indicate (cm^3 $molecule^{-1}$ s^{-1}, kcal mol^{-1} units):

$$k_1(300\text{-}800 \text{ K}) = (2.07 \pm 0.42) \times 10^{-10} \exp(-(2990 \pm 95)/RT)$$

[†] This chapter does not contain an abstract; its Table of Contents, as given here, fulfills this function.

[‡] Publication of these results in Journal of Chemical Physics is planned.

TABLE I
300–345 K MEASUREMENTS OF Al/NF$_3$ RATE COEFFICIENT

Mode[a]	P (Torr)[b]	$\bar{v}$ (m s^{-1})	[NF$_3$] (10^{13} cm^{-3})	T (K)	x_0 (cm)	k_1 (10^{-12} cm^3 molecule^{-1} s^{-1})	σ
F4	5.9	14	0.9– 5.7	335	+2	2.43	0.31
A4	8.8	14	0.7– 6.9	340	−2.1	2.33	0.71
F4	2.9	16	1.3– 8.1	320	+0.2	1.72	0.55
F1	17.7	19	1.0–25.0	340	+1.5	1.68	0.62
F3	5.0	21	2.0– 9.5	304	−1.2	1.81	0.25
F2	9.7	21	0.8– 6.3	335	−1.4	1.79	0.41
F2	3.8	23	1.3– 6.6	314	−1.0	1.94	0.16
F1	10.3	33	2.4–54.0	332	+0.7	1.51	0.16
F4	6.2	34	1.5–25.0	325	−2.5	2.32	0.52
A1	6.2	38	3.3–34.0	345	+2.7	1.62	0.28
F1	6.6	41	2.7–56.0	332	0.0	1.50	0.18
A1	11.1	41	1.7–38.0	345	−2.3	1.69	0.79
F2	3.2	43	0.8–11.2	314	−1.6	2.26	0.74
F1	2.0	46	1.1–25.7	300	+0.2	2.22	0.38
F2	3.0	46	1.5–29.0	314	+0.3	2.03	0.32
F1	6.2	46	1.5–49.0	315	−1.2	1.51	0.37
F2	8.2	49	1.0–13.5	316	−4.0	1.87	0.36
F2	2.9	50	1.3– 9.7	313	−2.3	2.25	0.30
F4	11.7	50	0.5–46	340	−4.0	1.96	0.36
F1[c]	6.3	60	1.6–23.0	331	−2.1	3.45	0.50
F2[c]	11.0	68	1.6–31.0	321	−1.0	2.68	0.59
F2[c]	5.5	71	0.9–20.0	320	−1.0	1.97	0.40
F3[c]	5.3	74	2.3–11.5	320	−4.0	3.18	0.46
F2[c]	3.6	75	0.6–10.3	325	+2.5	5.64	1.35
F2[c]	3.6	79	0.5–13.0	340	+2.2	2.36	0.98
A1[c]	11.9	85	1.3–51.4	332	−2.5	4.84	0.45
A1[c]	12.0	86	3.8–47	340	+2.3	6.32	0.56
F1	6.0	45	0.9–19.5	450	−2.2	7.13	0.65
F1	6.7	82	1.2–11.5	490	−3.2	8.04	0.91
F1	9.3	13	0.6– 9.9	510	0	10.8	1.2
F1	39.8	10	1.1–12.9	560	+0.5	17.5	2.1
F1	10.2	70	1.2–14.5	570	−0.7	14.3	3.2

TABLE I (continued)

300-345 K MEASUREMENTS OF Al/NF₃ RATE COEFFICIENT

Mode[a]	P (Torr)[b]	$\bar{v}$ (m s^{-1})	$[NF_3]$ (10^{13} cm^{-3})	T (K)	x_0 (cm)	k_1 (10^{-12} cm³ molecule^{-1} s^{-1})	σ
A1	20.8	36	0.3-9.4	606	-1.0	16.0	3.0
A1	5.5	37	0.4-8.1	640	-1.3	20.9	3.0
A1	5.4	29	0.2-2.2	721	+0.4	23.8	2.8
A1	20.2	17	0.1-3.5	727	0	26.2	4.3
A1	5.5	41	1.3-9.4	752	-3.2	31.2	6.2
A1[d]	20.4	16	0.1-2.2	807	-0.5	30.1	12.0
A1[d]	10.5	31	0.4-5.4	845	-1.5	21.4	13.3
A1[d]	20.8	39	0.6-6.2	852	+1.3	18.1	10.9
A1[d]	10.5	36	0.2-10.3	977	+2.4	20.2	15.4

[a] The letters A or F indicate whether the k_1 measurement was made in absorption or fluorescence, respectively, and the numbers indicate the wall surface: 1 = alumina; 2 = BaF₂-coated aluminum; 3 = HF-treated aluminum; 4 = stainless steel. 1, 2, and 3 are 2.54 cm i.d., 4 is 3.13 cm i.d.

[b] 1 Torr = 133.3 Pa.

[c] Affected by apparent flow velocity dependence; not used to determine overall $k_1(T)$ fit.

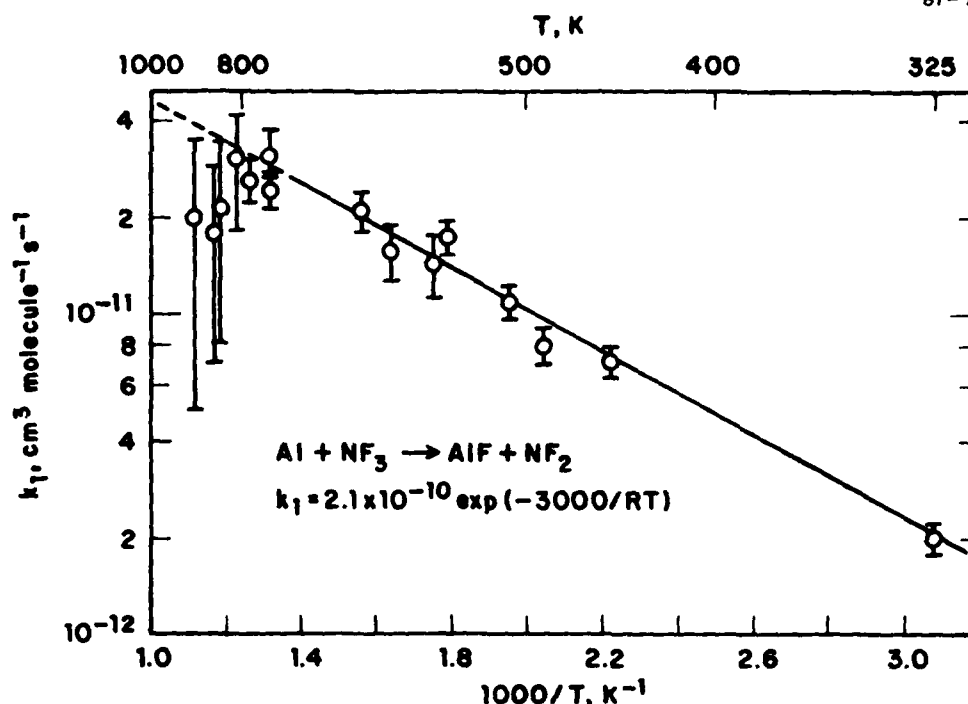[d] Affected by NF₃ thermal decomposition; not used to determine overall $k_1(T)$ fit.

FIGURE 1   TEMPERATURE DEPENDENCE OF RATE COEFFICIENT OF Al + NF₃ REACTION

Error bars are one standard deviation. Point
shown at 325 K represents 19 measurements.

It will be noted (Table I), that a great many experimental measurements were made at low (300-345 K) temperatures. These data were thought, upon initial interpretation, to be complicated by an apparent dependence of k_1 upon flow velocity, $\bar{v}$, and possibly upon NF₃ purity. At the same time, k_1 appeared independent of pressure (P), [Al], and [NF₃] in this limited temperature range.

The NF₃ used in these experiments was made available by Kelly Air Force Base. The manufacturer, Air Products and Chemicals, Inc., supplied a complete analysis with each cylinder. Initial measurements with the original batch (cylinder 1) were considered unreliable because of O_2 and N_2F_2 impurities in the NF₃. The 0.8 mol % O_2 present would contribute 2×10^{-13} cm³ molecule^{-1} s^{-1} to the apparent rate coefficient for Al consumption based on the rate coefficient of the Al/O_2 reaction of $(3 \pm 2) \times 10^{-11}$ cm³ molecule^{-1} s^{-1}. The cylinder also contained 0.2 mol % N_2F_2; nothing is known of the rate coefficient of the Al/N_2F_2 reaction. If it were on the order 3×10^{-10} cm³ molecule^{-1} s^{-1}, this reaction alone could be responsible for the remainder of the observed Al removal rates. This cylinder (1) was therefore returned to Air Products and Chemicals where part of its contents was purified. The

purified NF_3 (cylinder 2) had only 0.15 mol % O_2 and 0.012 mol % N_2F_2; however, it contained 0.17 mol % F_2O (as compared to 0.027 mol % in cylinder 1) which could equally lead to rate coefficient measurement falsification. NF_3 from cylinder 2 was therefore further purified by placing a Pyrex tube, filled with Linde Molecular Sieve 13X and having Pyrex wool plugs on either end, in the flow line. This reduced the N_2O content to < 0.01 mol % as verified by gas chromatography (gc) using a 7 m long 0.6 cm i.d., stainless steel column containing Waters Associates 80-100 mesh Porapak Q at room temperature. The gc measurement also showed no evidence for N_2F_2 or other active fluorides; either the column or the purification tube would probably have removed such compounds even if present in detectable quantities.[5]

The effects of these purifications were then tested by making k_1 measurements near 300 K as follows:

  (i)   Cylinder 2 (purified) with the Molecular Sieve 13x.

  (ii) Cylinder 1 (original batch) with the Molecular Sieve 13x
        and a $(KI + Na_2S_2O_3 \cdot 5H_2O)$ trap to remove active fluorides.[5]

  (iii) Cylinder 2 with the purification train of item (ii).

The results of these three sets of measurements were indistinguishable thus eliminating NF_3 purity as the cause of the apparent velocity dependence. For the remainder of the k_1 measurements, the method of item (iii) was used.

Surface decomposition was therefore suspected of causing the velocity dependence. To investigate this possibility, several different wall surfaces (in addition to the usual alumina) were used: these included stainless steel, HF-etched aluminum, and BaF_2-coated aluminum. Of these, only the BaF_2-coated walls gave k_1 data which appeared independent of flow velocity, but these data were complicated by a possible large temperature dependence. All of this work was carried out in the stationary inlet mode[6] in which the relative metal atom concentration, $[Al]_{rel}$, is measured optically as a function of the NF_3 added to the flow through the stationary inlet. Rate coefficients are obtained from the slope of the plot of $\ln[Al]_{rel}$ against $[NF_3]$; i.e., $-d \ln[Al]_{rel}/d[NF_3] = k_1 t$, where t is the reaction time determined from the flow tube distance proportionality, $t = x/\eta \bar{v}$. The distance, x, is that between the inlet and observation plane, and η is a flow profile factor ranging from 1.0 for plug flow to 1.6 for fully-developed laminar flow (parabolic profile). In HTFFR work, $\eta = 1.3 \pm 10\%$ is appropriate.[6]

A detailed review of these data and additional measurements at both 300-345 K and higher temperatures strongly suggested that the initial conclusions, i.e., that the "velocity dependence" of k_1 and that the variation in k_1 with T found in the BaF_2-coated tube resulted from wall effects, were spurious. The analysis indicated instead that the data could be consistently interpreted in terms of an "inlet effect" described by Piper, Velazco, and Setser.[7] According to this interpretation, uniform mixing is not always obtained at the reagent inlet and thus the measured x is not necessarily appropriate for calculating the reaction time. Piper et al[7] give an empirical method for determining the effective x in which the values $-d \ln[Al]_{rel}/d[NF_3]$ obtained at various inlet positions are plotted against the measured inlet-to-observation plane distance. The straight line which is obtained intercepts the distance axis at the virtual mixing point, x_0. This value, x_0, is expected to be negative, although positive values were also observed in our work (cf. Table I). Such positive values can result from turbulence effects near the inlet where the Reynolds numbers may be as large as 2.4×10^4 and can be caused by NF_3 recirculation upstream in the flow.*

Treating the data in this way[7] yielded the rate coefficient values shown in Table I, which is arranged in order of increasing flow velocity. In the range 14-50 m s^{-1}, the data are apparently $\bar{v}$-independent, but above 50 m s^{-1} an apparent rate coefficient acceleration occurs along with a dramatic increase in data scatter. It is argued that this "high $\bar{v}$" data can be rejected based on the consistency of the lower $\bar{v}$ data and upon the fact that the most rational mechanism to account for the increase in observed k_1 values with $\bar{v}$ is one in which inlet turbulence effects cause Al to be lost at the cold walls at a high rate. Other mechanisms, based on the supposed instability of NF_3 in the 300-345 K range fail to account for this rise. This can be seen from the following arguments: Any proposed mechanism which requires that a secondary decomposition product be formed from NF_3 at the wall and that it react subsequently with Al in the gas phase at a more rapid rate than NF_3 itself, would show a decrease in k_1 with $\bar{v}$ (i.e., because the wall contact time decreases). On the other hand, a mechanism in which NF_3 is simply lost either by sorption or dissociation into unreactive fragments at the wall could show an increase in k_1 with increasing $\bar{v}$, consistent with the trend of the

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* Simple NF_3 back diffusion is insufficient to account for this effect.

observations. To test this latter mechanism, k_1 values were calculated based
on the experimentally observed values of $-d \ln[Al]_{rel}/d[NF_3]$ according to the
expression:

$$-d \ln[Al]_{rel}/d[NF_3] = k_1\{[1 - \exp(-k_w t)]/k_w\}$$

which results from the mechanism in which NF_3 is lost at the walls at a rate
k_w. No k_w value within a factor of three of the diffusion-limited value ($k_w = $
3.60 D, where D is the diffusion coefficient of NF_3 in Ar from Ref. 8) resulted
in removing the "$\bar{v}$ dependence." Thus, this mechanism is also not consistent
with the data, nor is it consistent with the observations of others who have
treated the compatibility of $NF_3(g)$ with various substances in the context of
rocket engine plumbing.[8] These studies report no measurable decomposition or
loss of $NF_3(g)$ on alumina or stainless steel surfaces at the temperatures of
the present work (300-345 K). Indeed, experience provides one of the strongest
arguments against such a loss mechanism since NF_3 is routinely handled and
stored at room temperature in a variety of containers without noticeable loss
and can be passed quantitatively through tubing and gas chromatographic columns.

These arguments thus suggested that the Al/NF_3 rate coefficient
measurement in the 300-345 K range is $(2.02 \pm 0.42) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
The range of conditions covered was P = 2.0 to 17.7 Torr, $\bar{v}$ = 14 to 50 m s^{-1},
variation in $[Al]_{rel}$ by a factor of $\approx$ 40, and $[NF_3] = 1 \times 10^{13}$ to 5×10^{14} cm^{-3}.
The error estimate attached to k_1 includes propagated random error and the
additional 10% systematic error attached to the use of $\eta = 1.3$.[6]

In view of the consistency of the above interpretation, experimental
measurements on k_1 were extended to the 400-1000 K range to elucidate the T
dependence. The results are shown in Arrhenius form in Fig. 1; the conditions
and results of the measurements are given in Table I. Particular attention
was given to the possibility that NF_3 thermal dissociation could affect the
kinetic measurements. Calculations based on the rate coefficient for homoge-
neous thermal decomposition of NF_3[8] indicated that temperatures up to $\approx$ 1000 K
would be accessible before a high degree of dissociation began to interfere
with the k_1 measurement. If surface effects were to dominate, it appeared[8]
that 600-800 K would be the upper limit to which k_1 could be measured. To
determine the accessible range, gas chromatographic measurements using a ther-
mal conductivity detector with the 7 m Poropak Q(80/100) column[5] were made in
which samples were collected and analyzed for NF_3 content after passage through

the HTFFR under the experimental measurement conditions. This amount was then compared with the amount of NF_3 added to determine NF_3 loss. The results, summarized in Table II, show a sharp onset in NF_3 loss near ≈ 800 K. The k_1 data show a corresponding decrease in experimental precision (cf. Table I) in the same temperature range. Based on this correspondence, it seems reasonable that the k_1 measurements can be considered valid to ≈ 800 K. The present data are insufficient to draw any firm conclusion on the fate of the NF_3. It appears that the NF_3 losses result in the generation of fragments which are less reactive toward Al than is NF_3 itself. Alternatively, it may be that some NF_3 simply reacts with the HTFFR wall above ≈ 800 K and does not further react. Thus, more NF_3 must be added to remove the Al, and the apparent rate coefficient decreases.

TABLE II

GAS CHROMATOGRAPHIC MEASUREMENTS OF NF_3 DECOMPOSITION

T (K)	P (Torr)[a]	v (m s^{-1})	$[NF_3]_i$[b] (10^{15} cm^{-3})	Residence Time (ms)	Number of Measurements	$[NF_3]_f/[NF_3]_i$[c]
978	10.5	36	1.0–4.0	1.1–4.3	8	$0.20_3 \pm 0.01_4$
850	25.0	40	2.0–5.1	1.1–3.7	7	$0.93_5 \pm 0.04_5$
840	10.5	35	2.0–4.5	1.1–4.4	8	$0.76_0 \pm 0.15_0$
810	20.4	15	1.0–4.0	2.6–10.3	8	$0.89_5 \pm 0.01_2$
750	20.5	16	1.0–4.0	2.4–9.6	7	$1.00_0 \pm 0.01_1$
625	6.5	10	1.0–4.0	3.8–15.4	7	$1.00_1 \pm 0.01_6$
600	5.8	40	1.0–4.0	1.0–3.9	8	$1.00_1 \pm 0.02_7$
450	25	10	1.0–4.0	5.1–15.3	7	$0.99_8 \pm 0.01_1$
320	10	12	2.0–8.9	6.4–12.8	6	$1.01_1 \pm 0.03_2$

[a] 1 Torr = 133.3 Pa.

[b] Input NF_3 concentration calculated from flow rates of all gases.

[c] Measured ratio of gas chromatographic peak heights for collected sample of NF_3 after passing through HTFFR ($[NF_3]_f$) to collected sample of input NF_3 ($[NF_3]_i$).

B. THE B/O$_2$ REACTION

Some experimental effort on this contract was devoted to finding a suitable vaporization method to produce atomic boron in HTFFRs.[9] Unlike spectroscopic studies with diffusion flames[10] the source requirements for HTFFR use are more stringent because of the larger range of pressures, temperatures, and flow velocities covered in HTFFRs. Several means for generating atomic B were tried in the present contract. These methods included rf and resistance heating of B-containing crucibles and thermal and microwave discharge dissociation of BCl$_3$ and/or B$_2$H$_6$. Within the time and funding available, none of these sources could be developed to the point of providing gas phase B reliably for kinetic studies. Both rf and resistance heating of B were taken to the point of melting the B, but boron attack on the crucible material (e.g., graphite, boron nitride) occurred. In addition, extensive gas discharges in the HTFFR resulted from using the rf heater at pressures up to 100 Torr. Such discharges would unduly complicate kinetic measurements. Investigation of the pyrolysis and microwave discharge methods indicated that small concentrations of B are produced near the source, but that transport of these atoms for reaction in an HTFFR would be quite difficult. These latter methods are useful for the preparation of boron-containing free radicals such as BCl (and BF if BF$_3$ gas were used) in which the Air Force has considerable interest.

C. THE Mg/O$_2$ REACTION

This highly endothermic reaction was investigated at 1900 K. Removal of Mg by O$_2$ was observed. The Mg was found to permeate the HTFFR walls and even after removing the source of Mg from the HTFFR, Mg atoms still remained in the gas phase. Thus the kinetic measurements were not reliable. It would be possible to study this reaction with a less permeable HTFFR wall. It should be pointed out that the study of this reaction is important both for understanding Mg atom kinetics and also for the information that it could provide about the bond strength of MgO.

D. O-AlO BOND DISSOCIATION ENERGY

Formation of Al$_2$O$_3$ smoke from rocket exhausts is a well recognized Air Force problem. One potentially significant species in such smoke formation is AlO$_2$. There is a major controversy regarding the O-AlO bond dissociation

energy, which is important to be clarified in this context. The JANAF tables[11] accept Farber's result[12] that $D(O-AlO) = 120 \pm 4$ kcal mol^{-1}. However, papers[13,14] have appeared that fairly convincingly demonstrate that this species cannot have been present under Farber's operating conditions. The more generally accepted view among high temperature chemists[15] is that this bond energy cannot exceed 100 kcal mol^{-1}. However, this view contradicts our observation that the rate coefficient of the reaction $AlO + O_2 \rightarrow AlO_2 + O$ (measured by AlO disappearance, as observed by laser-induced fluorescence) has no temperature dependence, which implies[16] that $D(O-AlO) \gtrsim D(O-O) = 118$ kcal mol^{-1}. Additional evidence for our observations could come from observing other AlO reactions. While the study of such reactions was not a major objective under under the present contract, we did make some observations on AlO disappearance in the AlO/CO_2 reaction, for which we obtained data indicating a rate coefficient of $\approx 3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at $T = 750$ K. A preexponential of 3×10^{-10} cm^3 $molecule^{-1}$ s^{-1} would appear to be an absolute upper limit for this reaction, hence $\exp(-E_a/RT) \gtrsim 1.0 \times 10^{-4}$ and $E_a \lesssim 13.7$ kcal mol^{-1}. Since[11] $D(O-CO) = 127$ kcal mol^{-1}, it follows that $D(O-AlO) \gtrsim$ 113 kcal mol^{-1}, consistent with our earlier measurement of $\gtrsim 118$ kcal mol^{-1}, but not with the 100 kcal mol^{-1} value. Other work (not supported by this contract) on the Al/SO_2 reaction[17] indicates that $D(O-AlO) \gtrsim 126$ kcal mol^{-1}.

IV. CONCLUSIONS AND RECOMMENDATIONS

Progress in improving the performance of rocket and ramjets depends in part upon accurate data on reaction rate coefficients and mechanisms to allow model calculations on the location and nature of important heat release steps and to understand the routes to the ultimate formation of exhaust particulates. Modification of fuels and oxidizers to alter, e.g., performance or particulate formation, proceeds from a qualitative and quantitative grasp of the interplay of these chemical steps and the governing thermal and fluid dynamic conditions.

HTFFRs, because of their wide temperature range and their ability to study the reactions of refractory species involved, are currently the only experimental devices capable of providing the fundamental chemical kinetic data required. The present work shows the need to develop HTFFR methods further to allow generation of and measurements on more highly refractory species such as B and to address the problem of wall effects. Both of these are, in part,

materials problems. In addition, mechanistic pathways need to be clarified
for more complex reactions, for example, subsequent processes involving the
AlF formed in the Al/NF$_3$ reaction which was studied here. This involves the
development and installation of more versatile diagnostics for molecular
species, such as mass spectrometers or wide wavelength range lasers, to realize
the fuller potential of HTFFR methods.

V. PROFESSIONAL PERSONNEL

The principal investigator on this contract for approximately 80% of its
life was Dr. Arthur Fontijn; for the final 20%, Dr. William Felder assumed
this role. In addition, Dr. Dennis M. Manos and Mr. James J. Houghton contrib-
uted significantly to the work.

VI. PRESENTATIONS

Dr. Fontijn presented papers on the subject of measurement of the kinetics
of metal atom oxidation reactions in HTFFRs at:
1. AFOSR 1977 Combustion and Plume Kinetics Meeting, AEDC, Arnold AFS,
   TN (April 1977).
2. Third International Symposium on Plasma Chemistry, Limoges, France
   (July 1977).
3. Electrochemical Society Symposium on Metal Halide Chemistry, Atlanta,
   GA (October 1977).
4. Physics Department, Georgia Institute of Technology, Atlanta, GA
   (October 1977).
5. Quantum Institute, University of California, Santa Barbara, CA
   (October 1977).
6. North Jersey Section, American Chemical Society, Newark, NJ
   (November 1977).
7. AFOSR/AFRPL 1978 Rocket Propulsion Research Meeting, Lancaster, CA
   (April 1978).
8. Chemical Engineering Department, Princeton University, Princeton, NJ
   (May 1978).

9. The *Symposium* on "Current Status of Kinetics of Elementary Gas Reactions: Predictive Power of Theory and Accuracy of Measurement," NBS, Gaithersburg, MD (June 1978).

10. Gordon Conference on High Temperature Chemistry, Wolfsboro, NH (August 1978).

11. Tenth Materials Research Symposium on "Characterization of High Temperature Vapors and Gases," NBS, Gaithersburg, MD (September 1978).

12. Army Ballistics Research Laboratory, Aberdeen Proving Ground, MD (November 1978).

13. American Physical Society Symposium on "Atoms and Molecules in Flames and Plasmas," Chicago, IL (March 1979).

14. AFOSR/AFRPL 1979 Rocket Propulsion Research Meeting, Lancaster, CA (March 1979).

Dr. Felder discussed HTFFR techniques and measurements at:

1. AFOSR/AFRPL 1980 Rocket Propulsion Research Meeting, Lancaster, CA (March 1980).

2. Army Ballistics Research Laboratory, Aberdeen Proving Ground, MD (May 1980).

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